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DOI:

[10.1016/j.egypro.2019.01.709](https://doi.org/10.1016/j.egypro.2019.01.709)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Huang, Y, Xie, C, Li, C, Li, Y & Ding, Y 2019, 'Rheological behaviour and aggregation kinetics of EG/water based MCNT nano-suspension for sub-zero temperature cold storage', *Energy Procedia*, vol. 158, pp. 4846-4851. <https://doi.org/10.1016/j.egypro.2019.01.709>

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Checked for eligibility: 23/05/2019

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10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Rheological behaviour and aggregation kinetics of EG/water based MCNT nano-suspension for sub-zero temperature cold storage

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Abstract

EG-water based MCNT nano-suspensions were prepared by two-step method. Both experimental work and theoretical analysis were carried out to investigate the rheological property of prepared samples at different volume fraction and temperatures. The results showed that the experimental viscosity value could be matched well with the modified K-D model considering effective volume fraction of aggregations. In addition, this work exhibited an interesting trend of the behaviour of the viscosity vs shear rate curve when temperature is dropping down. A particle aggregation transformation mechanism were proposed to reveal the relationship between MCNT aggregation conditions and temperature, furthermore to explain the variety of shear behaviour of nano-suspensions.

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Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: nano-suspension, MCNT, rheological behavior, viscosity, phase change materials, cold storage.

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1. Introduction

Cold storage technology includes storing cold thermal energy to a medium and then releasing it from that medium for later usage. Such a technology has wide applications, like air conditioning[1], refrigerated vehicles[2], cryogenic power generation[3] and so on. Li et al.[4] has provided a detailed review for cold storage materials for sub-zero applications. In the review, Ethylene glycol (EG) and water mixture is considered an ideal heat transfer fluid for cold storage applications due to its varying freezing point below zero. Also, Kumano et al. [5] reported that EG-water has good potential in cold storage applications when compared with other organic alcohol aqueous solutions. Among properties of cold storage material, viscosity is very important because it could affect pressure drop and hence pumping power and convective heat transfer of a fluid flows. There have been numerous studies on the area and they are summarized in the following according to the effects of particle shape, particle size, volume fraction and particle aggregation on nanofluids' viscosity[6][7][8][9][10].

This work focuses on the rheological properties of EG-water based MCNT nano-suspension at a wide temperature range covering both ambient and sub-zero temperature. The reason of using EG-water based MCNT is that there are already a lot of research works about EG-water-CNT system[11], which lays a foundation for the sample preparation of our work. However, this work first studied the rheological properties of EG-water based CNT nano-suspension at sub-zero temperature and proposed a methodology for linking MCNT aggregation structure with the rheological behaviors. This work not only fills the research gap on rheology of nano-suspension, it also provides a promising way to predict other properties of nano-suspension related with particle structure.

2. Experimental methods

2.1. Materials and preparation

In this work, MCNT with >98% carbon basis, 10 nm outer diameter, 4.5 nm inner diameter and 3~6 μm length (CAS 308068-56-6) and ethylene glycol (EG) with purity of 99.5% (CAS 107-21-1) were purchased from Sigma Aldrich. Distilled water was obtained from an lab water still (Calypso water still, Fistreem International Ltd). To maintain the stability of the nano suspension, SDBS (CAS 9000-01-5, Sigma Aldrich) was used as surfactant.

The two-step method for preparing nano suspension is a process by dispersing nanoparticles into base fluids and it was applied in this work[12]. Firstly, EG and water were mixed at the ratio of 25/75 as basefluid. Then, a certain amount of MCNT corresponding to volume fraction and the same amount of SDBS was dispersed into the mixture of EG and water and stirred by a magnetic stirrer for 10 min. After that, the pre-processed nano composites were further treated continuously for 1 h using an ultrasonication probe. The sample preparation procedure is shown in Fig.1. The volume fraction of MCNT were 0.0625%, 0.125%, 0.25% and 0.5% respectively and the mass of added MCNT were calculated correspondingly as following:

$$\varphi = \frac{m_{MCNT}/\rho_{MCNT}}{(m_{MCNT}/\rho_{MCNT}) + (m_b/\rho_b)} \quad (1)$$

where φ represents the volume fraction of nano-suspension, m_{MCNT} and m_b are the mass of MCNT and base fluid respectively, ρ_{MCNT} and ρ_b determine the density of the MCNT and base fluid respectively.

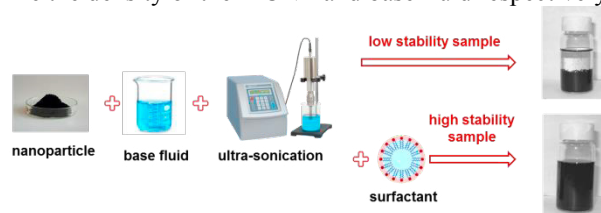


Fig.1. schematic of sample preparation.

2.2. Rheological investigation

An Anton Paar MCR 502 rheometer was used in this work to measure the dynamic viscosity of the EG-water

based MCNT nano colloidal. Measuring cell was parallel plate (L-PP35/CTD) with diameter of 35 mm. The viscosity of MCNT nano colloidal at different volume fractions (0.0625-0.5%) was measured at a linear increasing shear rate from 100 to 800 s⁻¹ at 25 °C, -5 °C, -10 °C and -15 °C respectively. Then the measured data were compared with the theoretical values predicted from some well-known models, see Table 1. A thermostat TC 30 temperature control unit was used to control the temperature of the samples including a heating furnace and a cooling liquid nitrogen evaporating unit. Value of 1 mPas was obtained at 25 °C for distilled water, and it kept constant with shear rate from 100 to 1000 s⁻¹, this indicates the accuracy of rheological properties measured by this rheometer.

Table 1 list of classical models used for viscosity of nano-suspension.

Model	Expression	Remarks
Einstein[13]	$\eta = \eta_0(1 + [\eta]^*\varphi)$	Applicable for relatively low particle concentration suspensions in which particles are spherical and non-interacting
Batchelor[8]	$\eta = \eta_0(1 + [\eta]\varphi + k_H[\eta]\varphi^2)$	Applicable for semi-dilute suspensions in which interaction of pair-particles are considered. k_H is Huggin's coefficient
Krieger-Dougherty[14]	$\eta = \eta_0(1 - \frac{\varphi}{\varphi_m})^{-[\eta]\varphi_m}$	Full range of concentration of particles with φ_m the maximum particle packing fraction
Modified Krieger-Dougherty[15]	$\eta = \eta_0 \left(1 - \frac{\varphi_a}{\varphi_m}\right)^{-[\eta]\varphi_m}$ $\varphi_a = \varphi \left(\frac{r_a}{r}\right)^{3-D}$	Aggregation of particles are considered, r_a and r are the radii of the cluster of particles and primary particle respectively, D is the fractural index

3. Results and discussion

3.1 Temperature effect on viscosity and shear behaviour

relative viscosity data of nano-suspension samples against volume fraction at 25 °C, -5 °C, -10 °C and -15 °C are plotted in Fig.2. It is obvious that at different temperatures, viscosity increasement of the same sample with same particle volume fraction are different as well. To find out how temperature affect rheological property, we used the modified K-D model with varying R value to fit the effective viscosity of samples at different temperatures. Results shows that the fitted R value are 5, 16, 25 and 26 at 25 °C, -5 °C, -10 °C and -15 °C respectively, which means that the effective volume fraction of EG-water based nano fluid increases with decreasing temperature. It is also worth to mention that when temperature decreases to some point, in this case is -10 °C, R value stops increasing enormously as it does at higher temperature. It means that the effective volume of the aggregation stops growing larger. The reason of the decelerating growth of aggregation probably is that the particles have formed some kind of saturate and stable structure at that low temperature. And the low diffusivity of particles due to high viscosity of EG-water base fluid at near freezing temperature maybe another reason for limited aggregating of MCNT.

The viscosities of EG-water based MCNT nano-suspension against shear rate at various volume fraction have been measured with decreasing temperature from 25 to -15 °C. The results are shown in Fig.3. One can see that at 25 °C, all EG-water based MCNT samples behave like newtonian fluid. However, when temperature decreases to -5 °C, it is obviously shown in Fig.3 (b) that 0.25 % and 0.5 % samples turn to be shear-thickening from 400 s⁻¹, while viscosities of other samples still keep constant with increasing shear rate. Then the temperature was further cooled to -10 °C, in Fig.3 (c), the curves of low volume fraction samples (0.0625% and 0.125%) start to bend upwards, but the 0.25 % and 0.5 % curves become declining with shear rate contrarily. Finally, samples were chilled to -15 °C which is only several degrees upper than the freezing point and viscosity data were plotted in Fig.3 (d). It is interesting that all nano colloids unanimously present a shear-thinning behavior in the end. This variety of rheological behavior of nano fluids at different temperatures could be contributed to the transformation of microstructure of the MCNT aggregation during cooling. We will discuss the detail of this proposed mechanism in the following section.

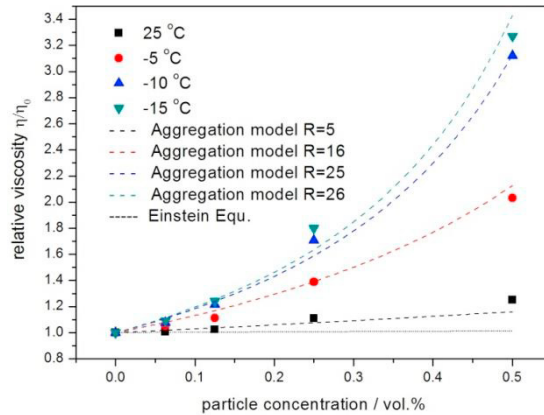


Fig.2. relative viscosity vs MCNT volume fraction at different temperatures.

3.2 Linking rheological behaviour with MCNT aggregation structure

The main reason of deviation of viscosity and shear behaviour at different temperature is supposed to be the formation of special particle aggregation structures. The prediction of the schematic of the temperature induced particle aggregation structure is illustrated in Fig.4. To simplify the drawing and make it clear to understand, we used round circle to represent MCNT particles, red arrow to represent shear force. Fig.4 (a), (b) and (c) demonstrate three different kinds of particle dispersion condition respectively corresponding to three different types of shear behaviour, thus Newtonian, shear thinning and shear thickening.

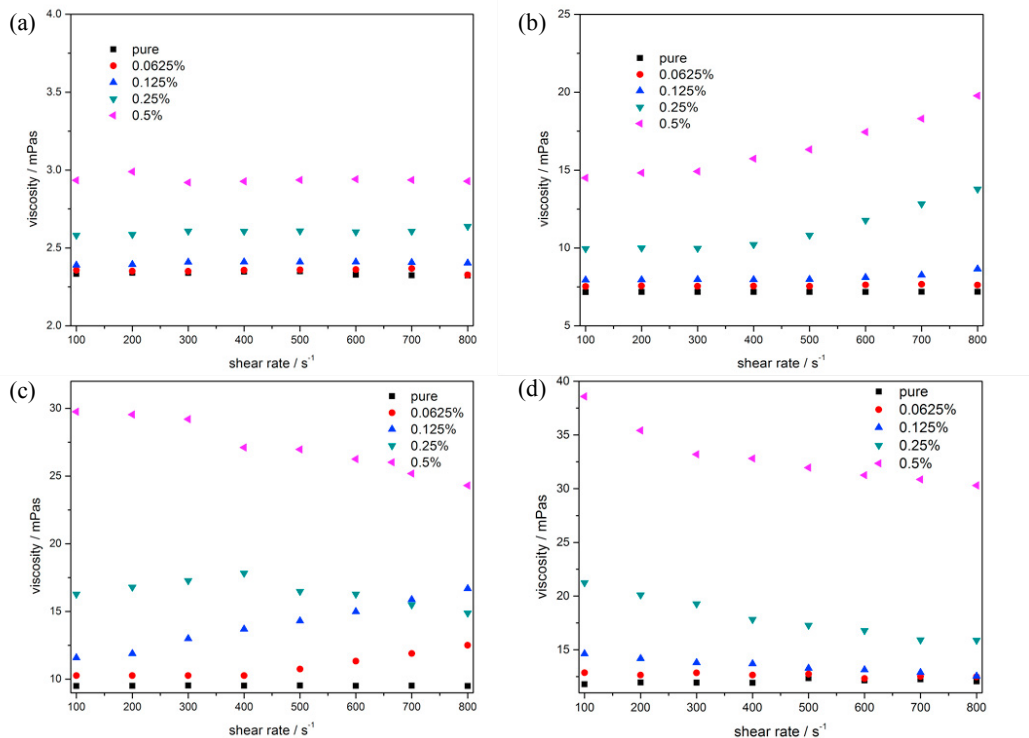


Fig.3. viscosity vs shear rate curve of EG-water MCNT nano-suspension at (a) 25 °C, (b) -5 °C, (c) -10 °C, (d) -15 °C.

According to Fig.4, the Newtonian behaviour could be explained that because particles are always kept away under the combination effect of Brownian motion and shear flow, the relative viscosity does not change with shearing. This is the reason of why we observe flat curves in Fig.3 (a). When temperature is decreasing, the intrinsic viscosity of EG-water base fluid will increase exponentially, thus limits the diffusivity of Brownian motion, therefore particles will clog together under shear flow. As a result, the total effect of rheological behavior will be increasing viscosity with increasing shear rate, namely shear-thickening behavior as shown in Fig.3 (b). When temperature reaches certain point, in this case is -10°C , particles are mostly aggregated together which could be demonstrated from fitted result in Fig.2. At this condition, we assume that aggregation of particles composites both strongly formed cluster and weak inter-cluster bond represented as dotted line as shown in Fig.3 (c). Therefore, increasing shear force will help breaking the inter-cluster bond and forming smaller effective volume, thus leads to the overall shear thinning behaviour as shown in Fig.3 (c) and (d).

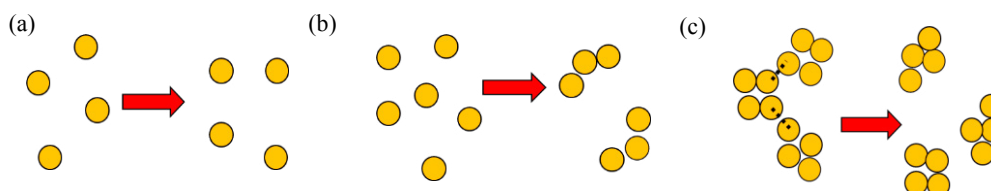


Fig.4. Particle transformation under shear flow for (a) Newtonian, (b) shear-thickening and (c) shear-thinning behaviour of EG-water based MCNT nano-suspension.

4. conclusions

In this paper, experimental work was conducted and theoretical analysis were applied. With the aims to understand the relationship between particle aggregation structure and rheological properties of EG-water based MCNT nano-suspension and to fill the research gap about nano-suspension at sub-zero temperature range, a series of stable samples were prepared using a two-step method and the following conclusions have been drawn:

- Classical models considering no particle aggregation fail to predict the experimental value of EG-water based MCNT nano-suspension, while modified K-D model introduced the aggregation and concept of effective volume fraction which is applicable to fit the experimental value.
- Higher particle volume fraction and lower temperature will cause larger aggregation of particles in the nano-suspension which are demonstrated by analysing relative viscosity with modified K-D model.
- Different types of structure of MCNT at different temperature are proposed to explain Newtonian, shear-thickening and shear thinning behaviours of nano-suspension. By predicting the structure of MCNT at different conditions, we can further predict other properties of nano-suspension such as thermal conductivity, which gives this methodology very useful potential in the future researches and applications.

Acknowledgements

This research is supported by the UK Engineering and Physical Sciences Research Council (EPSRC) under grants EP/P004709/1, EP/P003435/1, EP/L019469/1, EP/F060955/1, EP/L014211/1 and EP/K002252/1, the British Council under 2016-RLWK7-10243, China Scholarship Council (CSC), and a USTB grant for UoB-USTB joint Centre.

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